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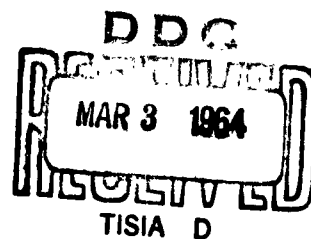
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Annual Report

STUDIES OF
COMPLEX PERCHLORATES

ONR Nonr 3943 (00)



February 10, 1964



Annual Report

STUDIES OF COMPLEX PERCHLORATES

ONR Nonr 3943 (00)

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February 10, 1964

Callery Chemical Company
Callery, Pennsylvania

Annual Report

TABLE OF CONTENTS

	Page
SUMMARY	1
INTRODUCTION	2
SUMMARY OF PREVIOUS RESEARCH	2
DISCUSSION OF RESULTS	4
I. New Compounds	4
Attempted Synthesis of New Hexaperchloratoaluminates	5
Potassium hexaperchloratoaluminate	5
Magnesium perchloratoaluminates	6
Hydrasinium hexaperchloratoaluminate	6
Guanidinium hexaperchloratoaluminate	7
Tetraperchloratoaluminates	8
$\text{NO}_2\text{Al}(\text{ClO}_4)_4$	8
$\text{NH}_4\text{Al}(\text{ClO}_4)_4$	11
Attempted synthesis of $\text{LiAl}(\text{ClO}_4)_4$	13
Attempted synthesis of $\text{KAl}(\text{ClO}_4)_4$	13
Attempted synthesis of $\text{C}(\text{NH}_2)_3\text{Al}(\text{ClO}_4)_4$	14
Complex Zinc Perchlorates	14
$\text{NO}_2\text{Zn}(\text{ClO}_4)_3$	14
$\text{LiZn}(\text{ClO}_4)_3$	16
$\text{NH}_4\text{Zn}(\text{ClO}_4)_3$	16
Complex Titanium Perchlorates	17
Attempted Synthesis of Complex Chromium Perchlorates	18
Miscellaneous Synthesis Chemistry	19
Possible mixed complexes	19
Complex chlorides of titanium	20
Complex chlorides of aluminum	21
II. Properties of Complex Perchlorates	21
Standard Heats of Formation	23
Densities	24
Hydrolytic Stability	25
Thermal Stability	27
Solubilities	33
Impact Sensitivity	34

Annual Report

SUMMARY

Results of continuing investigations of complex perchlorates are reported. Four new compounds, $\text{NH}_4\text{Al}(\text{ClO}_4)_4$, $\text{NO}_2\text{Al}(\text{ClO}_4)_4$, $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ and $\text{LiZn}(\text{ClO}_4)_3$ were prepared in good purity, while a less pure complex of titanium $((\text{NO}_2)_2\text{Ti}(\text{ClO}_4)_4)$ was synthesized. Various properties of these and other available compounds were studied.

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COMPLEX PERCHLORATES

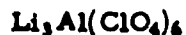
INTRODUCTION

This report contains a discussion of results obtained in an ONR program (Nonr 3943(00)) dealing with complex perchlorates. This work is a continuation of research originally sponsored under AF 33(616) 6382. Current studies have the overall objective of characterizing this class of compounds, and has involved measurement of various properties as well as synthesis of new representative compounds. Mr. Richard Hansen is the technical monitor of the program.

SUMMARY OF PREVIOUS RESEARCH

The Air Force sponsored program yielded several new compounds as well as techniques for their preparation. In addition, the new compounds were partially characterized. At this point we shall summarize chiefly the preparative methods, and will discuss various properties in the ensuing sections, since it will be appropriate to present, in the body of this report, properties of all known compounds for comparative purposes.

The following compounds were prepared in good purity.

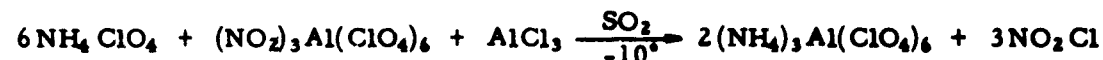
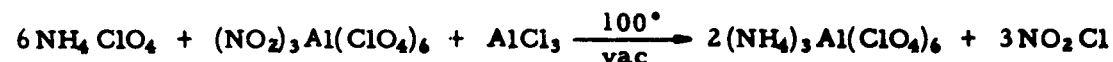
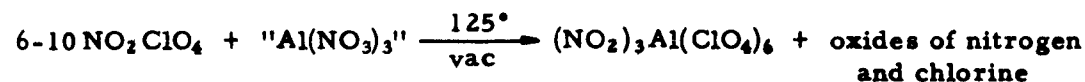
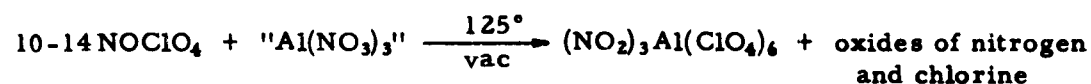
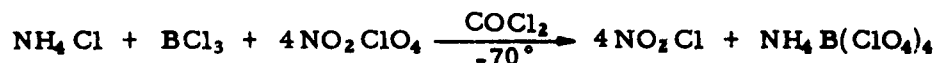
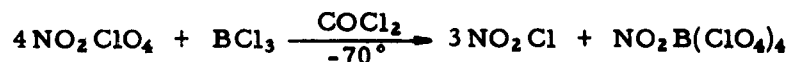
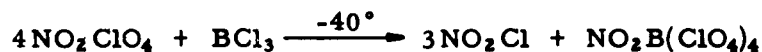
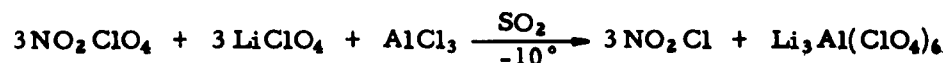
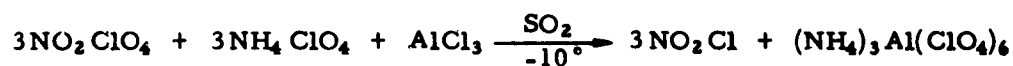
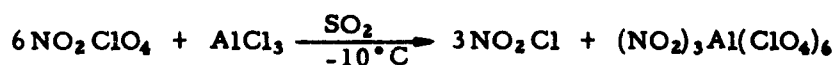


Annual Report

Materials of lower purity are shown below.



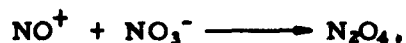
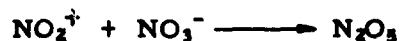
Preparative methods are indicated briefly by the following equations:



The basic reaction in a majority of the preparative schemes is elimination of halide as nitryl chloride, and this under appropriate conditions is accompanied

Annual Report

by formation of the complex perchlorate. Reactions in the "aluminum nitrate" systems are more complex; a major reaction is believed to be neutralization of nitrate by nitronium or nitrosonium ion



and excess nitrosonium perchlorate or nitronium perchlorate decomposes to oxygen and oxides of nitrogen and chlorine.

DISCUSSION OF RESULTS

I. New Compounds

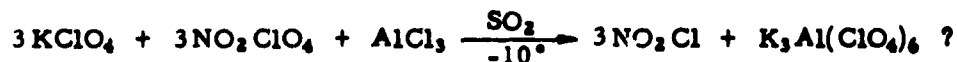
Attempted synthesis of new compounds constituted a major portion of the total effort. Suggested compounds were selected primarily on the basis of fundamentally interesting structural properties; in general a group of compounds representing a variety of combinations of central elements, of cations, and of coordination number were desired. New central elements of interest were titanium, a transition element such as chromium, and a dipositive element such as zinc. Suggested cations were potassium, magnesium and fuel bearing cations such as the guanidinium and hydrazinium ions. These possibilities were all investigated, with varying success as can be seen from the ensuing discussion.

Annual Report

Attempted Synthesis of New Hexaperchloratoaluminates.

Efforts in this direction met with limited success. The results were typified generally by what appeared to be a willingness to form the desired products, but an inability to either prepare products of high purity or products uncontaminated by the parent perchlorate, e. g. potassium perchlorate. No obvious explanation for the difficulties was usually apparent. It is felt that the failure to prepare new derivatives is not an indication that the proposed compounds are inherently unstable or structurally impossible, and is due primarily to limitations of the preparative procedures. These limitations are adverse solubility relationships, difficulty in preparing sufficiently pure reagents, and in some cases oxidative reactions involving nitronium perchlorate and full-bearing cations.

Potassium hexaperchloratoaluminate--Efforts to prepare this compound by the reaction



yielded white to yellow solids with analyses comparing favorably with theory. Found (mat/g): Al - 1.35, 1.34; K - 3.98, 4.08; total Cl--7.78, 7.69; Cl^- - 0.19, 0.11; N--0.18, 0.24. Theory: Al - 1.35; K - 4.05; Cl - 8.10. X-ray diffraction patterns revealed the presence of potassium perchlorate in addition to an unknown material. On this basis it must be assumed that the desired complex was not synthesized.

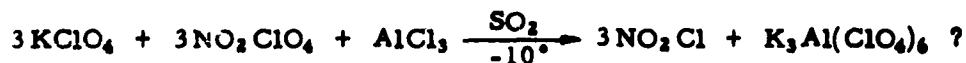
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Annual Report

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Annual Report

In other work efforts to prepare $\text{KAl}(\text{ClO}_4)_4$ were apparently successful. This compound is soluble in sulfur dioxide, while the materials described above were insoluble. This suggests the possibility that $\text{K}_3\text{Al}(\text{ClO}_4)_5$ may have formed, and failed to react further with potassium perchlorate due to its insolubility.

Magnesium perchloratoaluminates--Several attempts to prepare either $\text{Mg Al}(\text{ClO}_4)_3$ or $\text{Mg}_3\text{Al}_2(\text{ClO}_4)_{12}$ by reactions in sulfur dioxide involving appropriate quantities of magnesium perchlorate, nitronium perchlorate, and aluminum chloride were unsuccessful. Elimination of chloride as nitryl chloride was incomplete, and perchlorate contents of the products were substantially less than theoretical. Again, magnesium perchlorate was a constituent of the products.

Extraction of one of these products with sulfur dioxide yielded a soluble material with a new x-ray pattern which later proved to be that of $\text{NO}_2\text{Al}(\text{ClO}_4)_4$. This was the first experimental evidence for tetraperchloratoaluminate complexes.

Hydrazinium hexaperchloratoaluminate--Low purity products were prepared under the previous contract. Efforts to improve upon the earlier results were unsuccessful. The synthesis reaction was



Annual Report

Recoveries of nitrogen charged as $N_2H_5^+$ were only about 85%, and perchlorate contents of the products were low. It is probable that the hydrazinium ion was partially oxidized.

Guanidinium hexaperchloratoaluminate--Attempts to prepare $(C(NH_2)_3)_3Al(ClO_4)_6$ by reaction in sulfur dioxide of aluminum chloride with guanidinium perchlorate and nitronium perchlorate appeared to give straightforward reactions. Products exhibited a unique x-ray pattern, and analytical data were quite good save for apparently anomalous (high) carbon and hydrogen values.

Analytical Data

Mat/gram

	<u>Experiment</u>		<u>Theory</u>
Al	1.23	----	1.24
N	11.1	12.0	11.2
Total Cl	7.13	7.06	7.46
Cl ⁻	0		
C	5.22	4.77	3.73
H	28.1	27.6	22.3
N, as $[NO_3^- \text{ or } NO_2^+]$	0		

The above elements account for 98+% of the products, indicating little contamination with impurities, and the purity appears to be good save for carbon and hydrogen contents. Similarly high carbon and hydrogen values were obtained for guanidinium perchlorate, and no better results were achieved with another sample of guanidinium perchlorate prepared from silver perchlorate and guanidinium chloride.

Annual Report

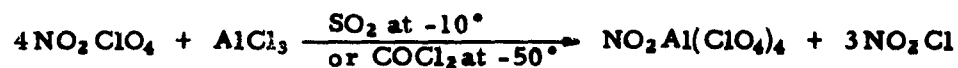
Material balances for nitrogen were quite good in the preparative reactions, and this tends to eliminate the possibility that high carbon and hydrogen values are due to oxidation of the guanidinium ion. Although the analytical data is somewhat suspect, it is believed that unexplained impurities in the guanidinium perchlorate are the source of the anomalous results. In spite of this uncertainty it is felt that the prepared products possess adequate, if not highly satisfying purities, and that high purity $(C(NH_2)_3)_3Al(ClO_4)_4$ can be prepared readily with high purity guanidinium perchlorate as a reagent.

Tetraperchloratoaluminates

Previous experience with the reaction system $NO_2ClO_4 - AlCl_3$ had lead to the conclusion that hexaperchloratoaluminates were preferred complexes from a stability standpoint. Further, it had been assumed that the tetraperchlorates were so unstable that rearrangement to hexaperchlorate complexes and decomposition products of aluminum perchlorate would occur spontaneously. These assumptions have in part proved to be erroneous, as indicated below.

$NO_2Al(ClO_4)_4$ -- As mentioned earlier, this compound was first obtained in small quantity by extraction of a material in which the intended product was a complex magnesium aluminum perchlorate. This interesting result led to further investigations of systems oriented toward $Al(ClO_4)_4^-$ derivatives. The compound $NO_2Al(ClO_4)_4$ has been prepared in good purity from the reaction

Annual Report



The product is quite soluble in sulfur dioxide, and if on occasion purification is necessary it can be accomplished readily by extraction. Typical analytical data are presented below.

	Analytical Data			
	Mat/gram			
	<u>Experiment</u>			<u>Theory</u>
Al	2.12	2.10	2.14	2.12
N	2.35	2.50	2.40	2.12
Total Cl	8.02	8.23	8.30	8.48
Cl ⁻	0	0.17	0.04	0
NO ⁺	0	0	0	0

The compound is a white, shock insensitive (>300 kg-cm) solid. Density as measured by displacement of Kel-F oil is 2.34 g/cc. It appears to be stable indefinitely at room temperature. As expected, it is thus more stable than $\text{NO}_2\text{B}(\text{ClO}_4)_4$, since the central element in the latter complex is considerably smaller than aluminum. Its thermal stability is substantially less than that of $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_4$. Differential thermal analysis yielded a large exotherm at 111°C as compared to an exotherm at 170°C for $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_4$. The x-ray diffraction pattern of $\text{NO}_2\text{Al}(\text{ClO}_4)_4$ is unique, but strikingly similar to that of $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_4$. Upon heating overnight at 50°C the x-ray pattern changes to that of $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_4$. This again indicates a preference for hexacoordination.

Annual Report

Nitromethane dissolves $\text{NO}_2\text{Al}(\text{ClO}_4)_4$ without apparent reaction, but evaporation of nitromethane yields a gummy solid from which solvent can be removed only by evacuation for long periods of time at about 50°C . It is believed that nitromethane strongly solvates the complex, perhaps with two moles occupying the fifth and sixth coordination position, although quantitative data to this effect has not been obtained.

Reaction of dinitrogen tetroxide with $\text{NO}_2\text{Al}(\text{ClO}_4)_4$ yields a gummy solid containing nitrosonium perchlorate by x-ray analysis. The other constituents could not be adequately defined by x-ray analysis. The basic reaction is believed to be



accompanied by decomposition of nitronium perchlorate to nitrosonium perchlorate and rearrangement-decomposition of " $\text{Al}(\text{NO}_2)_3$ " to nondescript polymeric aluminum oxynitrates.

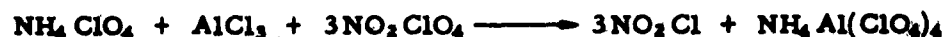
The standard heat of formation of $\text{NO}_2\text{Al}(\text{ClO}_4)_4$, as calculated from heats of hydrolysis is -110 ± 5 kcal/mol. The enthalpy of the reaction



is thus about -25 kcal, which is another indication of the greater inherent stability of the hexacoordinate complex.

Annual Report

$\text{NH}_4\text{Al}(\text{ClO}_4)_4$ -- Several reaction systems were investigated with approximately equal success. These are indicated by the equations below. All reactions employed sulfur dioxide at -10° as a solvent.



Reactions involving nitronium perchlorate resulted in clear solutions from which white solids were obtained on evaporation of the solvent. Evacuation to remove last traces of solvent resulted in pale yellow solids which were amorphous to x-ray.

Separation of insoluble silver chloride from the soluble complex was effected by filtration. The silver perchlorate reaction has the advantage that products are uncontaminated by NO_3^- or NO_2^+ , but even so product purities were generally less satisfactory than purities of products obtained with nitronium perchlorate. Typical analytical data are presented below.

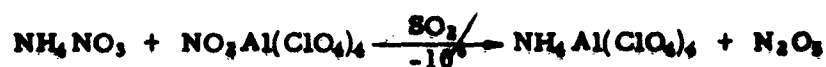
Analyses, mat/gram

	<u>Experiment</u>		<u>Theory</u>
	<u>From AgClO_4</u>	<u>From NO_2ClO_4</u>	
Al	2.22	2.29	2.26
NH_4	2.51	2.59	2.26
Total Cl	8.44	8.70	9.04
Cl^-	0	0.09	
N as NO_2^+ or NO_3^-	0	0.08	

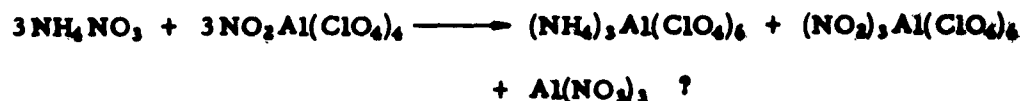
Annual Report

These data indicate borderline purity, particularly from the standpoint that about 3% of the products are unaccounted for. Sulfur was not detected, indicating the absence of sulfite or sulfate, and an adequate explanation of deviations from theory is not available.

An attempt to prepare $\text{NH}_4\text{Al}(\text{ClO}_4)_6$ by the reaction



was unsuccessful. The reaction system did, however, yield products of interest. The white crystalline solid exhibited the x-ray pattern of $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$, and analytical data indicated no loss of nitrogen by evolution as oxides of nitrogen. The analysis thus corresponded closely to that of the charge. The reaction appears therefore to consist of rearrangement, and if one assumes that ammonium ion is completely converted to $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$, the reaction may be represented by the equation



Aluminum nitrate is an unlikely product, and mixed nitrate-perchlorate complexes are considered more probable, as for example $\text{NO}_2\text{Al}(\text{NO}_3)_2\text{ClO}_4$. The formation of $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$ is another indication of preference for hexacoordinacy.

The compound $\text{NH}_4\text{Al}(\text{ClO}_4)_6$ is insensitive to shock (>300kg-cm), and has a density of 2.20 g/cc. It appears to be stable indefinitely at room

Annual Report

temperature, and hydrolyzes readily in the atmosphere. Significant exotherms are exhibited by DTA at 88-103°C (+4°C in magnitude) and 218°-245° (+6°C), and a slight endotherm occurs at 182°C. With moderate heating samples exhibit the x-ray pattern of $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$.

The heat of formation of $\text{NH}_4\text{Al}(\text{ClO}_4)_4$ as determined from heats of hydrolysis is -202 ± 4 kcal/mole. From this value the following reaction



is calculated to be exothermic by about 10 kcal, and the tetracoordinate complex is on this basis less stable than the hexaperchlorate complex.

Attempted synthesis of $\text{LiAl}(\text{ClO}_4)_4$ --This compound could not be prepared by methods applicable to $\text{NO}_2\text{Al}(\text{ClO}_4)_4$ and $\text{NH}_4\text{Al}(\text{ClO}_4)_4$. Low purity products were invariably obtained, and these exhibited the x-ray pattern of $\text{Li}_3\text{Al}(\text{ClO}_4)_6$. It seems evident that when both cations are small and/or highly charged, stability is possible only through hexacoordination.

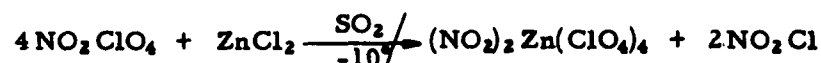
Attempted synthesis of $\text{KAl}(\text{ClO}_4)_4$ --Efforts to prepare this compound in high purity were not successful. Two experiments, one with NH_4ClO_4 - NO_2ClO_4 - AlCl_3 and the other with KAlCl_4 - AgClO_4 yielded sulfur dioxide soluble products with purities of 90-93% based on perchlorate content. These products were pale yellow, shock insensitive solids. It is expected that further careful studies would yield a high purity material.

Annual Report

Attempted synthesis of $C(NH_2)_3Al(ClO_4)_4$ --Unsatisfactory results were obtained, and analyses were again characterized by high carbon and hydrogen contents.

Complex Zinc Perchlorates

$NO_2Zn(ClO_4)_3$ --First efforts to prepare complex zinc perchlorates were based on the expectancy that the formal coordination number would be four, as in $(NO_2)_2Zn(ClO_4)_4$. Attempts to effect the reaction



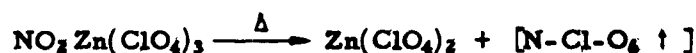
proved unfruitful, as elimination of nitryl chloride was very slow. Heating at 125° under vacuum of mixtures so obtained in sulfur dioxide yielded the compound $NO_2Zn(ClO_4)_3$ in very good purity.

	Analyses, mat/g		
	<u>Experiment</u>		<u>Theory</u>
N	2.41	2.49	2.44
Zn	2.46	2.42	2.44
Total Cl	7.31	7.29	7.32
Cl ⁻	0	0	
NO ⁺	0	0	

The white, crystalline, shock insensitive solid has a unique x-ray pattern. Its density, by displacement of Kel-Foil, is 2.7 g/cc. DTA traces show

Annual Report

slight endotherms at 60° and 178°, and a large exotherm at 197°C. The solid when heated in a sealed melting point capillary melted at 160°C. Very slow decomposition occurs at 125°C. After 6 days under vacuum at this temperature the composition of the residue was approximately that of zinc perchlorate.



Analytical data in mat/g for the product were: Found--Zn, 3.94; total Cl, 7.42; Cl^- , 0.19; N, 0.18. Theory for $\text{Zn}(\text{ClO}_4)_2$ --Zn, 3.79; Cl, 7.58. These analyses indicate a purity on a weight basis of 95-96% with the contaminants presumably being zinc chloride, zinc nitrate, and zinc oxide. The x-ray pattern of the material was that of an unknown compound.

The heat of formation, from heat of hydrolysis, of $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ is -48 ± 4 kcal/mole. This value is 20 to 30 kcal less negative than anticipated, since it indicates that the heat of formation of anhydrous zinc perchlorate is -45 to -50 kcal. This value is about the same as that of zinc iodide. Comparisons of heats of formations of metallic iodides and perchlorates show that the iodides normally are substantially less exothermic than corresponding perchlorates. The heat of formation of zinc perchlorate was on this basis expected to be -65 to -75 kcal, and that of $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ would then be within this range.

The compound $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ is hygroscopic in air, as are all of the complex perchlorates prepared to date. It is insoluble in sulfur dioxide but

Annual Report

readily soluble in nitromethane. No studies of reactivity have been made. It is anticipated that reactivity will be typical of compounds containing the nitronium ion.

LiZn(ClO₄)₃--This compound has been prepared in high purity in one gram quantities from lithium perchlorate, zinc chloride and nitronium perchlorate. The procedure consists of premixing the reactants in sulfur dioxide followed by removal of solvent and heating under vacuum for 48 hours at 125°C. The reactions are charged as indicated by the equation



Part of the excess nitronium perchlorate decomposes, and the remainder is collected as a sublimate. Found: Zn, 2.63; N, 0.14; Li, 2.69; total Cl, 8.0; Cl⁻, 0. Theory for LiZn(ClO₄)₃: Zn, 2.7; Li, 2.7; Cl, 8.08.

In larger scale runs the high purities have not been achieved, so quantities required for characterization are not available. Other preparative methods have been studied. The most promising of these consists of reaction in nitromethane as follows:



NH₄Zn(ClO₄)₃--Attempts to prepare this material have thus far been unsuccessful, as products invariably have contained ammonium perchlorate.

Annual Report

Complex Titanium Perchlorates

Research in this area has resulted in products corresponding closely to $(\text{NO}_2)_2\text{Ti}(\text{ClO}_4)_6$, and it is believed that this compound is indeed capable of existence. Products from reaction under various conditions, and with varying stoichiometries, of nitronium perchlorate with titanium tetrachloride were quite variable in composition, however, and usually exhibited significant reducing power toward ceric ion. The reducing power is probably due either to nitrite or nitrosonium ion. This in combination with variations in other analytical data indicates $[\text{Ti-O}]$ formation



and subsequent formation of nitrite or nitrate



Analytical data for three products are expressed by the formulae:



The reducing power toward ceric ion exhibited by these solids is arbitrarily expressed as NO^+ . Mass accountability for all three products was 99+% on the basis

Annual Report

of the above formulae. There is a good correspondence to the general formula M_2TiX_6 , which is indicative of a tendency to hexacoordination on the part of titanium.

The above solids as well as others exhibited an unknown x-ray pattern, and it is believed that the major constituent is $(NO_2)_2Ti(ClO_4)_4$. Maximum purity on this basis is 93-95%.

Reactions between nitronium perchlorates and titanium tetrachloride with few exceptions employed sulfur dioxide or phosgene as solvents. Some solubility was observed in sulfur dioxide, but efforts to increase purity by extractions were unsuccessful.

One can summarize experience with titanium as follows. Products close to $(NO_2)_2Ti(ClO_4)_4$ have been obtained, and this is believed to be the preferred specie. The nitronium perchlorate-titanium perchlorate reaction is, however, subject to side reactions which formally yield NO^+ and oxide (nitrate), and high purity is thus difficult to achieve.

Attempted Synthesis of Complex Chromium Perchlorates

First attempts to prepare compounds such as $(NO_2)_2Cr(ClO_4)_6$ involved chromic chloride and nitronium perchlorate as reactants. As may have been anticipated chromic chloride was for all practical purposes inert toward nitronium perchlorate. In sulfur dioxide at $-10^\circ C$ no reaction occurred. Chromic chloride was also recovered when mixtures with nitronium perchlorate were heated at $125^\circ C$.

Annual Report

Dehydration of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with 2, 2-dimethoxypropane yielded a material with the approximate composition of chromic nitrate. This material was intimately mixed with nitronium perchlorate and heated slowly to 100°C . In one experiment the reactants exploded, and from another a brownish, very shock sensitive solid was obtained. Research on chromium complexes was therefore terminated.

Miscellaneous Synthesis Chemistry

A few unusual though not necessarily new materials were prepared as possible intermediates in the synthesis of complex perchlorates. Some evidence of unique complexes was obtained, and the preparative methods are of general interest.

Possible mixed complexes--Potassium perchlorate and ammonium perchlorate exhibit very limited solubilities in sulfur dioxide. Both are readily solubilized by aluminum chloride in the proportion 1 AlCl_3 :1 MClO_4 . This has been construed as evidence of formation of the complexes $\text{NH}_4\text{AlCl}_3\text{ClO}_4$ and $\text{KAlCl}_3\text{ClO}_4$. It is of course equally possible that disproportionation to two soluble complexes may occur.



This in turn suggests the interesting possibility, one which has not been explored, that hexaperchlorato complexes could be prepared as follows.

Annual Report

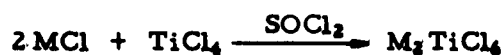


The complex chloride could be separated from the insoluble hexaperchlorato complex by filtration and washing.

Complex chlorides of titanium--Two materials were prepared.

One, $((\text{CH}_3)_4\text{N})_2\text{TiCl}_6$, is not unique in the chemistry of titanium. The other material appears to exhibit a coordination number of eight.

The method of Sandhu, Chakkal and Sandhu⁽³⁾



was used to prepare $((\text{CH}_3)_4\text{N})_2\text{TiCl}_6$. The pale yellow, sulfur dioxide soluble solid exhibited a unique x-ray pattern, and its purity was quite good. Reaction of the complex chloride with nitronium perchlorate ($6 \text{NO}_2\text{ClO}_4 : 1 ((\text{CH}_3)_4\text{N})_2\text{TiCl}_6$) in sulfur dioxide yielded a low purity material (based on $((\text{CH}_3)_4\text{N})_2\text{Ti}(\text{ClO}_4)_6$) which proved to be shock sensitive, and which contained $(\text{CH}_3)_4\text{NClO}_4$.

Attempts to prepare $(\text{NH}_4)_2\text{TiCl}_6$ by a similar route in either sulfur dioxide at -10° or phosgene at -75° yielded unreacted titanium tetrachloride and highly insoluble residues. Analytical data for these solids corresponded fairly closely with values for $(\text{NH}_4)_4\text{TiCl}_6$. One product, for example, is represented by $(\text{NH}_4)_{4.7}\text{TiCl}_{6.3}$. No ammonium chloride was evidenced by x-ray analysis, and efforts to remove ammonium chloride by extraction with sulfur dioxide were unsuccessful. The observed ratios do not suffice to precisely define the product, but the results overall indicate a pronounced tendency toward octacoordination.

(3) Sandhu, Chakkal and Sandhu, Jour. Ind. Chem. Soc., 37, No. 6, (1960)

Annual Report

$(\text{NH}_4)_2\text{Zn}(\text{NO}_3)_4$ --This compound was prepared in excellent purity by reacting $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ (from $\text{Zn} + \text{N}_2\text{O}_4$) with ammonium nitrate at 100°C under vacuum.



The x-ray pattern of the product was that of an unknown, indicating the absence of ammonium nitrate.

Complex chlorides of aluminum--The two compounds KAlCl_4 and NH_4AlCl_4 are readily prepared from the respective chlorides in sulfur dioxide. Both are quite soluble in this solvent.

II. Properties of Complex Perchlorates

Various physical and chemical properties of the complex perchlorates have been studied in order to further characterize this class of materials, and to provide a basis for correlating properties with composition and with structure.

Actual structures of the complex perchlorates can not at present be specified, as little evidence of the type required for definition of structure is available. Two questions are important: (1) what is the nature of the bonding between ClO_4 and other elements or ions (Al , Zn , Ti , NH_4 , NO_2), and (2) can one rightfully state that complex anions exist as units $(\text{B}(\text{ClO}_4)_4)^-$, $[\text{Al}(\text{ClO}_4)_6]^{3-}$, etc). Conclusive answers to these questions must await accumulation of data from x-ray and spectral

Annual Report

analysis, as well as supporting information derived from sources such as conductivity and transport studies. In the interim it has been assumed that the complex perchlorates are more nearly ionic than covalent in character, with the point of chief significance being the hypotheses that the ClO_4 group retains as much as possible the ionic character it prefers.

Whether this assumption is correct or not, there can certainly be little doubt that the stability of the complexes will be a function of the size and charge of the "central" atoms or ions. Complex perchlorates of boron are thus expected to be less stable than similar complexes involving the larger aluminum.

The question of the existence of discrete anions (e. g. $\text{Al}(\text{ClO}_4)_4^-$) may be appropriate only for solutions, since in crystalline solids the perchlorate groups or ions may be arranged symmetrically about both cationic elements, with the result that a charged, discrete anion ($\text{Al}(\text{ClO}_4)_4^{3-}$) has little actual physical significance. This of course would not be true if ClO_4^- were involved in strong covalent bonding. The fact that several complex perchlorates are readily soluble in non-aqueous solvents, while one of the constituent perchlorates (NO_2ClO_4 , NH_4ClO_4 , KClO_4) is insoluble, indicates that in solution $\text{NO}_2\text{B}(\text{ClO}_4)_4$, $\text{NH}_4\text{B}(\text{ClO}_4)_4$, $\text{NO}_2\text{Al}(\text{ClO}_4)_4$, $\text{NH}_4\text{Al}(\text{ClO}_4)_4$, $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ and $\text{KAl}(\text{ClO}_4)_4$ are ionized, with the anions being the complex anions inferred by the formulae, or dissolve without disseciation into ions of any type. The latter possibility seems highly unlikely.

One consequence of the assumption that ClO_4 prefers to retain its ionic

Annual Report

character applies to the two types of aluminum complexes. In $\text{Al}(\text{ClO}_4)_4^{3-}$ the average bond strength ($\text{Al}-\text{ClO}_4$) should be less than in $\text{Al}(\text{ClO}_4)_4^-$, with the result that the hexacoordinate complex should be thermodynamically more stable as well as more resistant to decomposition to aluminum oxides and chlorine oxides. This expectation has been verified by comparisons of heats of formation and of thermal stabilities. A discussion of various properties follows.

Standard Heats of Formation--These data were without exception calculated from heats of hydrolysis. Available data is tabulated below.

Standard Heats of Formation
of Complex Perchlorates

Kcal/mole/25°C

$(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6 : -120 \pm 5$	$\text{NH}_4\text{B}(\text{ClO}_4)_4 : -145 \pm 5$
$(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6 : -348 \pm 10$	$\text{NO}_2\text{B}(\text{ClO}_4)_4 : -80 \pm 10$
$\text{Li}_3\text{Al}(\text{ClO}_4)_6 : -414 \pm 10$	$\text{NO}_2\text{Al}(\text{ClO}_4)_4 : -110 \pm 5$
$\text{NH}_4\text{Al}(\text{ClO}_4)_4 : -202 \pm 4$	$\text{NO}_2\text{Zn}(\text{ClO}_4)_3 : -48 \pm 4$

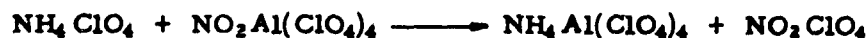
The hexaperchlorates of aluminum differ in enthalpy by amounts such that the general reaction



involves little or no change in enthalpy. This is usual in compounds of this type.

On the other hand, the enthalpy of the reaction

Annual Report



is -14 kcal, indicating a greater inherent stability for $\text{NH}_4\text{Al}(\text{ClO}_4)_4$. A similar comparison indicates that $\text{NH}_4\text{B}(\text{ClO}_4)_4$ is 12 kcal less "stable" than $\text{NO}_2\text{B}(\text{ClO}_4)_4$.

The heat of formation of $\text{NO}_2\text{B}(\text{ClO}_4)_4$ is open to question, however, due to impurities present in the sample used to measure heat of hydrolysis.

As mentioned earlier, the tetracoordinate aluminum complexes are inherently less stable than hexaperchlorate compounds, on the basis of heats of formation.

Densities--Densities have been measured by liquid displacement, usually with Kel-F oil.

Densities of Complex Perchlorates

Grams/cc

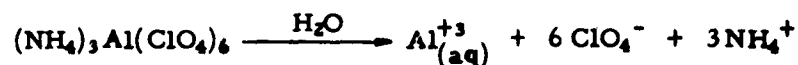
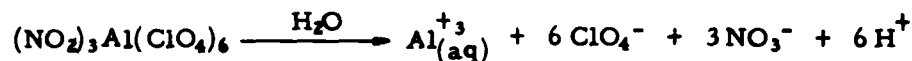
$(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$	2.35	$\text{NH}_4\text{Al}(\text{ClO}_4)_4$	2.20
$(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$	2.09	$\text{NO}_2\text{B}(\text{ClO}_4)_4$	2.26
$\text{Li}_3\text{Al}(\text{ClO}_4)_6$	2.48	$\text{NH}_4\text{B}(\text{ClO}_4)_4$	2.15
$\text{NO}_2\text{Al}(\text{ClO}_4)_4$	2.34	$\text{NO}_2\text{Zn}(\text{ClO}_4)_3$	2.70

The densities have a quasi-fundamental significance in that they are indicative of the apparent size or volume of various groups, and of the closeness of packing of ions or groups in crystal lattices. This is more apparent from molar volumes, which are : $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$ - 324 cc; $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$ - 329 cc;

Annual Report

$\text{Li}_3\text{Al}(\text{ClO}_4)_6$ - 254 cc; $\text{NO}_2\text{Al}(\text{ClO}_4)_4$ - 201 cc; $\text{NH}_4\text{Al}(\text{ClO}_4)_4$ - 201 cc; $\text{NH}_4\text{B}(\text{ClO}_4)_4$ - 199 cc; $\text{NO}_2\text{B}(\text{ClO}_4)_4$ - 201 cc and $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ - 152 cc. By appropriate comparisons it can be seen that the ammonium and nitronium ions appear to occupy the same volume in the complexes, and aluminum is equivalent to boron in volume effectively occupied. Further treatment on a molar volume basis indicates that the complex perchlorates are qualitatively "normal" compounds in that the aggregate cations exhibit the expected trend in apparent size or volume. The order of decreasing apparent "cation size", with simple cations included for purposes of comparison is NO_2^+ , Rb^+ , NH_4^+ , $((\text{NO}_2)_3\text{Al}/_6)^+$ and $((\text{NH}_4)_3\text{Al}/_6)^+$, $(\text{NO}_2\text{Zn}/_3)^+$, $(\text{NH}_4\text{Al}/_4)^+$, Na^+ , Li^+ , $(\text{Li}_3\text{Al}/_6)^+$ and $(\text{Mg}/_2)^+$. Zinc is a relatively small but heavy central cation, which accounts for the high density of $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$. In $\text{Li}_3\text{Al}(\text{ClO}_4)_6$ both lithium and aluminum are small so that high density results in spite of the low cation weight.

Hydrolytic Stability--All of the complexes dissolve readily in water with solvolysis to appropriate ions.



All are also susceptible to hydrolysis in air, and will in fact deliquesce.

Three compounds $((\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$, $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$ and $\text{Li}_3\text{Al}(\text{ClO}_4)_6$) were placed in a constant humidity (30%) box for extended periods of time to determine

Annual Report

rates of moisture pickup and if possible ascertain the nature of hydrolysis in air. One gram samples were placed in 2 ounce sample jars. The atmosphere was stagnant save for convection currents. Ammonium perchlorate and nitronium perchlorate were used as reference materials.

The increase in weight for $\text{Li}_3\text{Al}(\text{ClO}_4)_6$ and $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$ is initially linear with time, and both compounds absorb water at about the same rate. At 17-18% H_2O , $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$ begins to absorb water more slowly, while $\text{Li}_3\text{Al}(\text{ClO}_4)_6$ continues to absorb linearly up to at least 28% water. It thus appears that $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$ absorbs water at a uniform rate up to formation of ammonium perchlorate and $\text{Al}(\text{H}_2\text{O})_9(\text{ClO}_4)_3$. The lithium ion can be hydrated, so $\text{Li}_3\text{Al}(\text{ClO}_4)_6$ continues to absorb water at a uniform rate until both cations are solvated. As expected, analysis of hydrolysates of the lithium and ammonium derivatives indicated only absorption of water.

Hydrolysis of $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$ is somewhat more complicated, in that it formally consists of aquation of nitronium perchlorate and aluminum perchlorate.



Volatilization of one or both acids is a possibility, and weight changes are in themselves of little significance. Hydrolysis under conditions of these experiments led eventually (ca 200 hours) to complete volatilization of nitrogen as nitric acid, but perchloric acid was retained quantitatively in the hydrolysates.

Annual Report

In one set of experiments three samples of $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$ were analyzed, with sacrifice of the sample, after exposures of one day, three days and ten days. Throughout the first three days of exposure all samples were weighed frequently, usually every hour. These samples gained weight at a faster rate than other samples which were weighed only once or twice every 24 hours. (Figure I). Analytical data obtained upon analysis of the three samples is depicted in Figure II. Of particular significance is the fact that the data shows only a gain in weight from water absorption during the first three days. Thereafter, nitric acid evolves with additional absorption of water. The point at which nitric acid evolution begins is at about six moles of water per mole of $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$. This corresponds to hydrolysis to $3\text{HNO}_3 - 3\text{HClO}_4 - \text{Al}(\text{H}_2\text{O})_3(\text{ClO}_4)_3$. This suggests that during initial stages of hydrolysis the aluminum ion competes on equal terms with "nitronium perchlorate" for water, and that only after absorption of sufficient water for formation of $\text{Al}(\text{H}_2\text{O})_3^{+3}$, nitric acid and perchloric acid does incoming water become available for formation of H_3OClO_4 and release of nitric acid.

It is believed that the higher rate of water uptake for frequently weighed samples of $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$ than for infrequently weighed samples (Figure I) is due to mechanical exposure, in the weighing process, of fresh surfaces for contact with the gas phase.

Thermal Stability--On a qualitative basis the inherent stabilities of the complex perchlorates can be rated as follows in order of increasing stability:

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FIGURE I
HYDROLYTIC STABILITY
WEIGHT INCREASE WITH TIME

Constant Humidity Derived From $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

+ weighed every hour for 70 hours

± weighed once every 24 hours

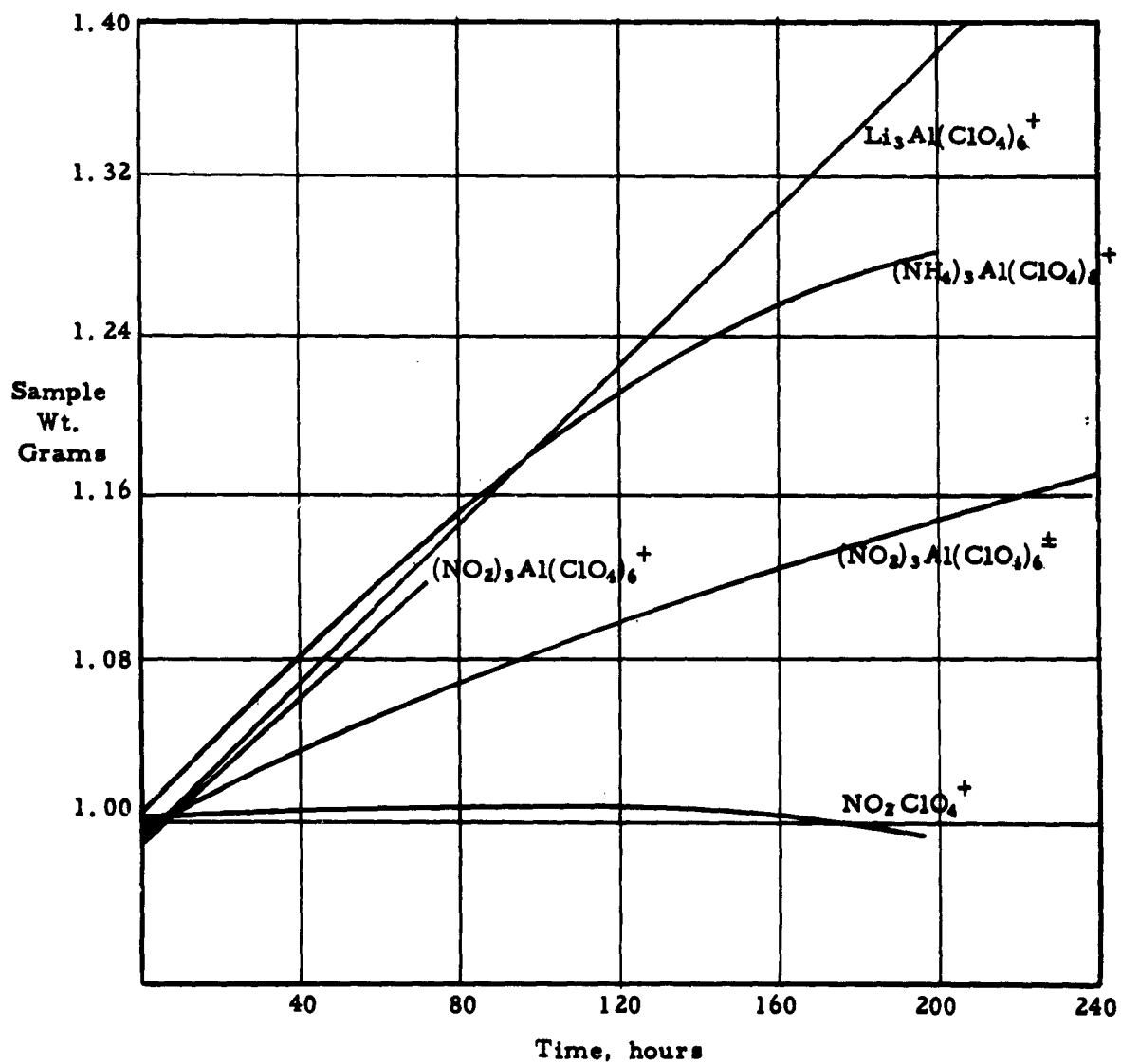
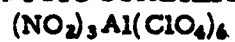


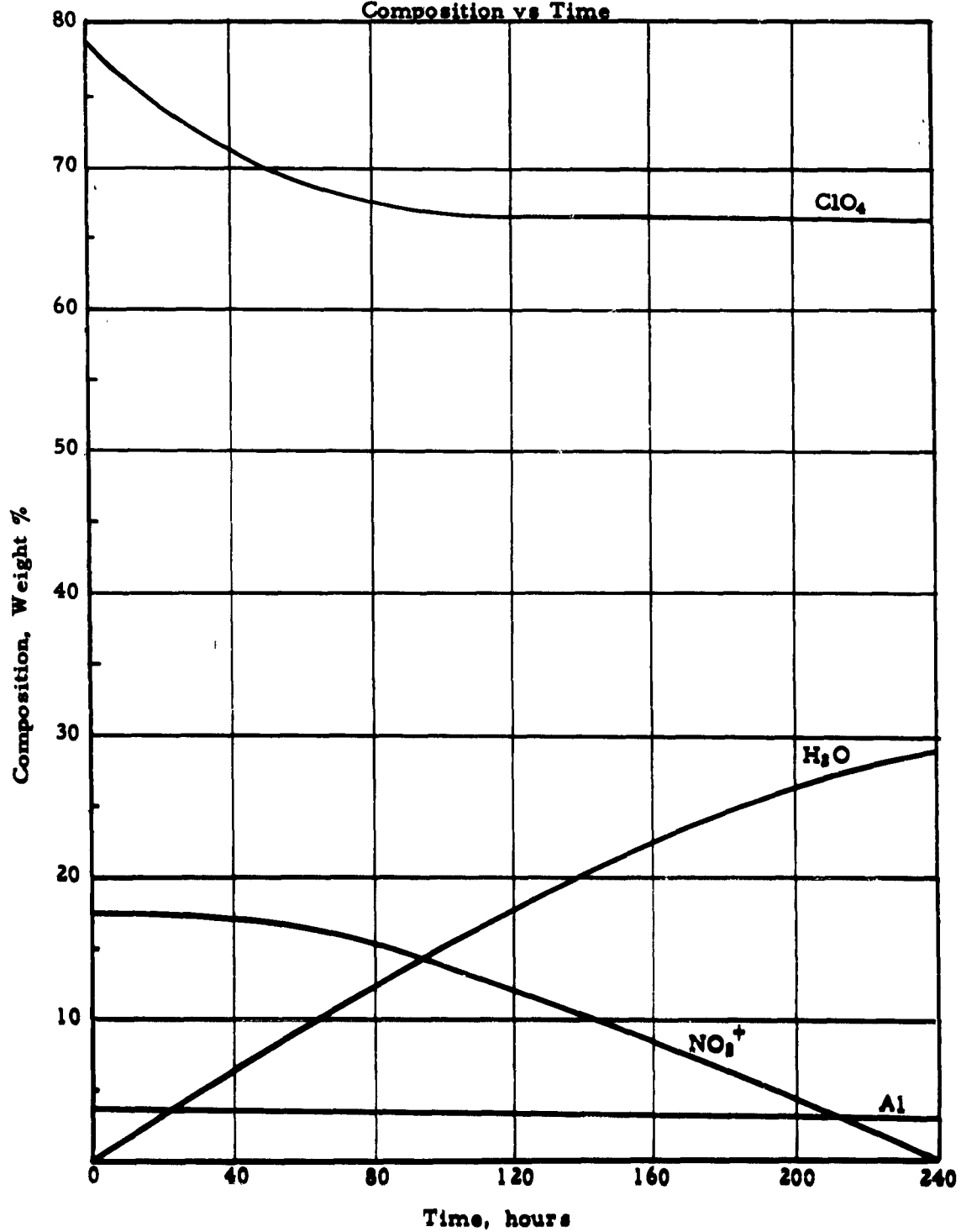
FIGURE II

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HYDROLYTIC STABILITY IN AIR



Composition vs Time



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$(\text{NH}_4\text{B}(\text{ClO}_4)_4, \text{NO}_2\text{B}(\text{ClO}_4)_4) < (\text{NH}_4\text{Al}(\text{ClO}_4)_4, \text{NO}_2\text{Al}(\text{ClO}_4)_4) < \text{NO}_2\text{Zn}(\text{ClO}_4)_3 < (\text{NO}_2)_3\text{Al}(\text{ClO}_4)_4 < (\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6 < \text{Li}_3\text{Al}(\text{ClO}_4)_6$. The stability of $\text{Li}_3\text{Zn}(\text{ClO}_4)_3$ is at least equal to that of $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ and should be considerably better. Stabilities may be compared more precisely as follows, with "slow" indicating days to weeks and "rapid" hours for significant decomposition.

	<u>Slow</u>	<u>Rapid</u>
$\text{NH}_4\text{B}(\text{ClO}_4)_4, \text{NO}_2\text{B}(\text{ClO}_4)_4$	ambient	70°-80° C
$\text{NH}_4\text{Al}(\text{ClO}_4)_4, \text{NO}_2\text{Al}(\text{ClO}_4)_4$	50-60°	90-110°
$\text{NO}_2\text{Zn}(\text{ClO}_4)_3$	120-130°	170-180°
$(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_4$	130-150°	170°
$(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$?	180-200°
$\text{Li}_3\text{Al}(\text{ClO}_4)_6$?	180-200°

Differential thermal analyses have been obtained for several of the compounds. This data is summarized below. Magnitudes of endotherms and exotherms are indicated in °C.

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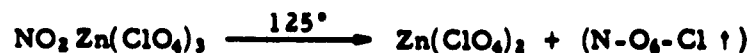
Differential Thermal Analyses

	<u>Endotherms</u>	<u>Exotherms</u>
$(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$	140°-150° (4°C)	170°-230° (45°C)
$(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6^*$	146° (0.5°C)	109°-124° (1°C) 211°-224° (1°C) 232°-257° (5°C)
$\text{Li}_3\text{Al}(\text{ClO}_4)_6$		100°-115° (2°C) 180° (1°C) 197° (10°C)
$\text{Li}_3\text{Al}(\text{ClO}_4)_6^{**}$	240° (1°C) 246° (3°C)	225°-233° (2°C)
$\text{NH}_4\text{Al}(\text{ClO}_4)_4$	182° (<1°C)	88°-103° (4°C) 218°-245° (6°C)
$\text{NO}_2\text{Al}(\text{ClO}_4)_4$		111° (large)
$\text{NO}_2\text{Zn}(\text{ClO}_4)_3$	60° <1°C 178° <1°C	197°-244° (16°C)

* One sample of $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$ exploded at ~ 100°, another at ~ 200°. Two samples yielded DTA traces up to the temperature limit of the apparatus.

** After heat soaking at 100°-105° for 100 hours.

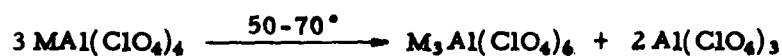
Modes of decomposition vary, and are to a large extent dependent on the stability of "parent" perchlorates at the temperature of decomposition. In only one instance has the simple perchlorate of the central atom been observed as a decomposition product.



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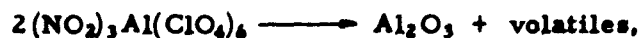
The complex perchlorates of boron decompose at moderately elevated temperatures, and nitronium perchlorate is a decomposition product of $\text{NO}_2\text{B}(\text{ClO}_4)_4$. Similarly ammonium perchlorate results from $\text{NH}_4\text{B}(\text{ClO}_4)_4$. With both compounds the decomposition proceeds toward boric oxide and NO_2ClO_4 or NH_4ClO_4 , with boron oxyperchlorates being probable intermediates in the decomposition.

The tetraperchlorates of aluminum, by way of contrast, decompose at moderate temperatures to the more stable hexaperchlorates, as evidenced by x-ray analyses.



Decomposition under conditions favoring this rearrangement has not been studied quantitatively.

One compound, $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$, differs from the remainder in that aluminum oxide is apparently the only stable decomposition product. One might predict that oxyperchlorates or oxynitrates would be relatively stable products, but this does not appear to be the case at temperatures (130° - 150°) required for significant decomposition in a few days time. Analyses of products obtained at 140° indicate that the decomposition is described by the equation



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and x-ray patterns confirm the presence of $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$ in residues. It is worthy of note that both $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$ and $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ are substantially more stable than nitronium perchlorate (Cordes, J. Phys. Chem. 67, 1693 (1963)), and this indicates that the "nitronium perchlorate" content of these two compounds is stabilized by coordination of perchlorate.

The remaining hexaperchlorates of aluminum $((\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$ and $\text{Li}_3\text{Al}(\text{ClO}_4)_6$) yield ammonium perchlorate and lithium perchlorate at temperatures of about 200°C. The decomposition reactions can thus be represented by



Quantitative studies of the decomposition of these compounds have not been conducted.

Solubilities--These have been determined only qualitatively. All compounds are soluble in water with hydrolysis. Three non-aqueous solvents, nitromethane, sulfur dioxide and phosgene have been tested with various compounds. Results are summarized below.

$(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$: insoluble in sulfur dioxide and phosgene. In nitromethane solvolysis occurs to yield highly soluble $(\text{NO}_2)_2\text{Al}(\text{ClO}_4)_5$ and insoluble NO_2ClO_4 . The product $(\text{NO}_2)_2\text{Al}(\text{ClO}_4)_5$ has not been obtained free of solvent.

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$(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_4$ and $\text{Li}_3\text{Al}(\text{ClO}_4)_4$: insoluble in sulfur dioxide and phosgene.

$\text{NO}_2\text{B}(\text{ClO}_4)_4$, $\text{NH}_4\text{B}(\text{ClO}_4)_4$: soluble in phosgene.

$\text{NH}_4\text{Al}(\text{ClO}_4)_4$, $\text{NO}_2\text{Al}(\text{ClO}_4)_4$: soluble in sulfur dioxide and nitromethane.

$\text{NO}_2\text{Zn}(\text{ClO}_4)_3$, $\text{LiZn}(\text{ClO}_4)_3$: insoluble in sulfur dioxide, soluble in nitromethane.

The term "soluble" as used above indicates more than a minimal solubility, as solubility was usually observed to the extent of at least one gram in 30-40 cc of solvent. Evidence of insolubility was obtained by efforts to extract the compound with the solvent in question.

Impact Sensitivity--Of the compounds prepared in high purity, only two ($\text{NO}_2\text{B}(\text{ClO}_4)_4$ and $\text{NH}_4\text{B}(\text{ClO}_4)_4$) were sensitive within the limits (300 kg-cm) of the Callery apparatus. The drop weight value (50% test) for $\text{NO}_2\text{B}(\text{ClO}_4)_4$ was 47.5 kg-cm. Complexes (impure) containing the tetramethylammonium ion were without exception sensitive to impact; of these, $(\text{CH}_3)_4\text{NE}(\text{ClO}_4)_4$ was most sensitive, being susceptible to initiation under handling conditions. Impure $(\text{N}_2\text{H}_5)_3\text{Al}(\text{ClO}_4)_4$ was relatively insensitive (170 kg-cm), while $(\text{C}(\text{NH}_2)_3)_3\text{Al}(\text{ClO}_4)_4$ was insensitive.

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